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PRODUCTION OF MAGNESIUM HYDROXIDE PRODUCTS FROM SALINE WASTEWATERS

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(56) Prior Art Documents
AU 641871 31132/93 C02F 9/00
ES 8505197
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(57) Claim

1. A process for the manufacture of magnesium-hydroxide slurry from unprocessed magnesium-containing inorganic saline wastewaters comprising the steps of:

(a) if required, placing the saline wastewater in a concentration adjustment pond or a tank and adjusting the concentration by dilution or evaporation to contain 5g/L to 100g/L magnesium ion in solution to allow formation of a precipitate;

(b) separating the supernatant from the precipitate;

(c) further adjusting the magnesium ion concentration in the supernatant from step (b) to 8-10g/L;

(d) if the sulphate content of the solution resulting from step (c) is more than 1.2g/L, reacting the solution from step (c) with either lime $[\text{Ca}(\text{OH})_2]$ or caustic soda $[\text{NaOH}]$ and centrifuging to remove solids;

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(e) reacting the resultant solution from step (c) or (d) as appropriate with either lime $[\text{Ca}(\text{OH})_2]$ or caustic soda (NaOH), first under rapid stirring and then slow mixing conditions to produce a slurry dominated by magnesium hydroxide.

(f) thickening the slurry thus produced in a cyclone or centrifuge; and

(g) dewatering the resultant magnesium hydroxide slurry.

AUSTRALIA

Patents Act 1990

COMPLETE SPECIFICATION FOR A PETTY PATENT

PRODUCTION OF MAGNESIUM HYDROXIDE PRODUCTS
FROM SALINE WASTEWATERS

THE FOLLOWING STATEMENT IS A FULL DESCRIPTION OF THIS
INVENTION, INCLUDING THE BEST METHOD OF PERFORMING IT
KNOWN TO ME:-

)
The present invention relates to a process for the
treatment of inorganic saline wastewaters to produce
magnesium hydroxide $[Mg(OH)_2]$ slurry and slurry powder
which may be used for application to wastestream
5 processing, as well as a cheap feedstock for
manufacture of magnesium metal and ceramic composites.

Agricultural, salt harvesting and mining operations,
as well as mineral processing, industrial and
10 municipal activities, particularly in arid and
semi-arid regions of Australia and elsewhere, produce
large quantities of waste bitterns and brines, which
contain significant concentration of magnesium ion in
solution. Currently, most of these liquid wastes are
15 regarded as a kind of wastewater and in inland areas
they are either stored through the use of retainment
and evaporation ponds, or disposed of via the sewerage
system. In coastal areas the bulk of waste bitterns
and brines generated from salt harvesting, mineral
20 processing and industrial operations are discharged to
tidal waterways or directly to the sea. Apart from
the potential pollution of inland and coastal
waterways and groundwater systems, the current saline
wastewater disposal practices exclude any major use of
25 such waters as a feedstock for the manufacture of

saleable products with environmental and industrial application and for revenue generation.

5 Magnesium hydroxide slurry for use as a flocculant in
wastewater treatment may be produced from magnesia
(magnesium oxide) powder which is presently available
in the Australian market. The magnesia may also be
used for electrolysis to produce primary magnesium
metal. However, this magnesia powder is produced by
10 the calcination of magnesite (MgCO_3) ore, and
consequently is expensive as the price of the magnesia
and its hydroxide derivatives reflects the inherited
costs associated with magnesite ore quarrying,
calcination, grinding and additional costs associated
15 with production of marketable magnesia products.

The high costs of the powdered magnesia has limited
the use of magnesium hydroxide flocculant in
wastewater processing, and other flocculants such as
20 alum, ferric chloride, poly aluminium chloride(PAC)
and acrylic amide are often preferred for this reason.

Australian Patent No. 641871 discloses a process for
production of magnesium hydroxide slurry from
25 inorganic saline wastewaters. In that process, feed
bittern undergoes multiple evaporation and cooling to
sub zero temperatures and the extraction of halite,
epsomite and carnallite salt mixture prior to
magnesium hydroxide slurry production.

30 It is an object of the present invention to disclose a
method for manufacturing of magnesium hydroxide slurry
and slurry powder products from magnesium ion
containing inorganic waste bitterns and brines which
35 process overcomes one or more of the disadvantages
with existing method of magnesium hydroxide production
from saline wastewaters, or at least offers

cost-effective alternative products for environmental and industrial application. A further aim of the invention relates to solving the problems associated with the storage and/or disposal of unprocessed saline wastewaters at the same time.

The present invention provides a process for the manufacture of magnesium hydroxide slurry from unprocessed magnesium-containing inorganic saline wastewaters comprising the steps of:

- (a) if required, placing the saline wastewater in a concentration adjustment pond or a tank and adjusting the concentration by dilution or evaporation to contain 5g/L to 100g/L magnesium ion in solution to allow formation of a precipitate;
- (b) separating the supernatant from the precipitate;
- (c) further adjusting the magnesium ion concentration in the supernatant from step (b) to 8-10g/L;
- (d) if the sulphate content of the solution resulting from step (c) is more than 1.2g/L, reacting the solution from step (c) with either lime $[\text{Ca}(\text{OH})_2]$ or caustic soda $[\text{NaOH}]$ and centrifuging to remove solids;
- (e) reacting the resultant solution from step (c) or (d) as appropriate with either lime $[\text{Ca}(\text{OH})_2]$ or caustic soda (NaOH) , first under rapid stirring and then slow mixing conditions to produce a slurry dominated by magnesium hydroxide.
- (f) thickening the slurry thus produced in a cyclone or centrifuge; and
- (g) dewatering the resultant magnesium hydroxide

slurry.

5 Preferred embodiments of the present invention will now be further described with reference to FIG. 1, which is a flow chart indicating the basic steps through which an appropriate feed bittern may be processed to produce magnesium hydroxide slurry and powder.

10 Feed solutions most suitable for the process are inorganic waste bitterns and brines which contain equal to or more than 5g/L magnesium ion in solution, and belong to one of the following saline water types in Eugster's classification scheme:

15 Na-(Mg)-Cl-(SO₄)
Na-(Mg.K)-Cl-(SO₄)
Na-(Mg)-Cl
Na-Cl

20 Australian saline wastewaters from salt harvesting operations and saline water disposal basins in arid and semi-arid regions, soda manufacturing factories, coal power station fly-ash stabilisation ponds and mineral processing operations can be potential
25 feedstock for the process disclosed herein, but commonly contain excessive concentration of sodium and chloride ions in dissolved form.

30 In the process of FIG. 1, excessive levels of sodium and chloride ions are removed by the precipitation of halite (NaCl) and other precipitates during the first step of the process, in which the feed solution is placed in a concentration adjustment tank or a pond and its concentration adjusted by evaporation or
35 mixing (where necessary) to typically contain 5g/L to 100g/L magnesium in the solution. The halite and other precipitates formed in this step are separated

and may be discarded.

5 The supernatant solution is then transferred to a
second concentration adjustment tank or a pond and its
magnesium concentration further adjusted to within
8-10g/L Mg^{2+} range by mixing with fresh water and the
sulphate ($SO_4^{=}$) content in the solution is determined.
Thenafter, depending on sulphate content, the liquor
10 is reacted either with calcium-hydroxide (lime) or
sodium hydroxide (caustic soda) following the process
steps identified under either Option "A" or Option "B"
in FIG. 1.

15 For a liquor with sulphate content of 1.2g/L or less
the process route under Option "A" is followed in
which the solution is reacted with lime or caustic
soda in a conversion tank, first under rapid stirring
conditions then using a slow mixer. This reaction
causes formation of a magnesium hydroxide slurry,
20 which is thickened and then dewatered to produce a
slurry containing 25-30% by weight of solids dominated
by $Mg(OH)_2$.

25 Compared with caustic soda, the use of lime is
preferred as it is the more cost-effective
alternative; other added advantages of lime addition
include a faster pH adjustment of the feedstock prior
to magnesium hydroxide precipitation, increased
settleability of the flocs produced and a more
30 effective removal of dissolved phosphorous species
from wastewaters which are treated with the magnesium-
hydroxide slurry thus manufactured.

35 As shown in FIG. 1, for adjusted liquors with sulphate
content of more than 1.2g/L, the process route under
Option "B" is followed. This process route includes
the additional steps of initial reaction of the

5 solution with lime or caustic soda and centrifuging to separate a sulphate dominated mineral waste. The supernatant is then reacted once more with lime or caustic soda, thickened and dewatered as described above for low sulphate feed, to produce a magnesium hydroxide slurry which is suitable for direct application to wastestream processing.

10 Depending on product quality requirements, the magnesium hydroxide slurry produced by process routes "A" or "B" can be subjected to one or more steps of washing (with freshwater) and dewatering which will then remove the bulk of soluble salts and thus increase the quality of the final product. The final
15 product is introduced to markets in vacuum packed water-proof containers.

20 Depending on chemical composition of the original feed solution used, the scheme of the present invention contemplates that recovery of additional salts will be possible by further processing of the filtrate from dewatering steps of magnesium hydroxide slurry production.

25 For production of magnesium hydroxide slurry powder, as shown in FIG. 1, the slurry product manufactured by following the above-described procedure is first dewatered by using a hydro-cyclone or a high-speed centrifuge to obtain a thickened slurry, containing
30 about 40% by weight $Mg(OH)_2$, then it is dried and powdered by mechanical means to give a final magnesium hydroxide slurry powder product. In arid areas with elevated evaporation rates, the process route for the production of magnesium hydroxide slurry
35 powder can be shortened significantly by direct evaporation to near dryness of the thickened slurry in a shallow evaporation pond. Alternatively, industrial

scale hot-air dust blower can be employed to produce a slurry powder product with certain prescribed particle size range. The final product is then vacuum packed in water proof containers prior to introduction to the markets.

Compared with the conventional magnesium hydroxide slurry products available in Australian markets, the products manufactured according to this invention offer a distinct market advantage because of their lower production costs. The availability of these products to the end users at relatively lower production costs results from a combination of the use of cheap and plentiful waste bitterns and brines as a raw feed combined with the simplicity of the manufacturing procedure. Added advantages of the magnesium hydroxide slurry and slurry powder products, according to the process disclosed herein, include easy product handling and safety of workers and environment and wide ranging options for the storage, handling and transport of the products.

Additionally, the use of inorganic saline wastewater for producing a range of saleable products, for revenue generation and waste minimisation, offers significant incentives to modify the current practices with the storage and/or disposal of unprocessed saline wastewaters.

The following Examples further illustrate preferred embodiments of the invention.

EXAMPLE 1

The feed solution was a chloride dominated waste bittern with low sulphate ($\text{SO}_4^{=}$) content, containing 124g/L magnesium, which was first diluted with

freshwater to adjust the magnesium ion content in the solution and allowed to settle out impurities. When analysed the adjusted feed contained 100.51g/L Magnesium, 2.49g/L Sodium, 0.22g/L Calcium, 0.41g/L Potassium, 0.18g/L Sulphate and 242g/L Chloride.

The feed solution was further diluted 10 times by adding freshwater and mixing properly. Then, following the processing steps for production of magnesium hydroxide slurry and slurry powder, shown in FIG. 1 under Option "A", the diluted feed was transferred to a conversion tank. Lime at a dose of 30g/L was introduced to the feed and mixed for about 10 minutes under rapid stirring conditions to produce a thin magnesium hydroxide slurry. This slurry was then transferred to a thickener and subjected to slow mixing for about 30 minutes, then dewatered using a cyclone which produced a slurry containing about 28.5% by weight solids dominated by magnesium-hydroxide.

The slurry thus produced was subjected to another round of dewatering by which a paste-like product containing about 40% by weight solids dominated by magnesium hydroxide was obtained. The resultant magnesium hydroxide paste was then artificially evaporated to near dryness and a hot-air dust blower was used to produce a powder product with particle size equal to or less than 60 microns. Microscopic examination, supported by results of chemical analysis and x-ray diffraction indicated a mineralogical composition for the final product being comprised of 70.5% Magnesium hydroxide $[Mg(OH)_2]$, 22.5% Halite (NaCl), 2.6% Calcium-chloride $(CaCl_2 \cdot nH_2O)$ with the balance of weight being largely water content.

EXAMPLE 2

The feed solution in this run was a sulphate-rich waste brine containing 51g/L Magnesium, 59g/L Sulphate and 190g/L Chloride in solution, which required no initial adjustment of magnesium ion concentration.

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Following the processing steps for Option "B", shown in FIG. 1, the feed solution was first diluted with freshwater until the magnesium^{ion} content in the solution was about 9.5g/L, then the solution was transferred to a conversion tank and lime at a dose of 8.9g/L was introduced to the feed and the compound mixed for about 10 minutes under rapid stirring conditions. After centrifuging and removal of the solids settled at the bottom of the tank, the supernatant was subjected to a second round of reaction with lime at a dose of 16.7g/L under slow mixing conditions for about 1 hour. The resultant slurry was then thickened for about 30 minutes in slow mixing vessel and then dewatered using a cyclone which produced a slurry containing about 25% by weight of solids dominated by magnesium hydroxide. The magnesium hydroxide slurry thus produced was then further processed according to steps shown in FIG. 1 and the procedure described in EXAMPLE 1, which produced a magnesium hydroxide slurry powder product with particle size of 60 microns and finer. Based on microscopic examination, supported by chemical analysis and x-ray diffraction of the final product, the composition of the final product was determined to be comprised of 66% Magnesium hydroxide $[Mg(OH)_2]$, 7.5% Gypsum $[CaSO_4 \cdot 2H_2O]$, 8.8% Calcium-hydroxide $[Ca(OH)_2]$, 3.7% Sylvite (KCl), 5.2% Halite (NaCl), with the balance of weight being largely water content. After twice washing with the freshwater and drying, the final slurry powder product gave 81% Magnesium hydroxide.

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EXAMPLE 3

In another run similar to that of EXAMPLE 1 the same feed solution was subjected to the process route for magnesium-hydroxide slurry and slurry powder production following the Option "A", shown in FIG. 1. However, in this trial for the conversion purpose instead of lime addition sodium hydroxide (NaOH) was introduced to the feed at a dose of 33g/L and the compound then mixed for about 10 minutes under slow stirring conditions. The procedure followed subsequently to produce magnesium hydroxide slurry and slurry powder were the same as described in EXAMPLE 1. Accordingly, following microscopic examination and confirmation of the findings by x-ray diffraction analysis results, the mineralogical composition for the final product was determined as being comprised of 80% Magnesium hydroxide [$\text{Mg}(\text{OH})_2$], 18% Halite (NaCl), 1.9% Calcium chloride ($\text{CaCl}_2 \cdot n\text{H}_2\text{O}$) with the balance of weight being water content.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the manufacture of magnesium-hydroxide slurry from unprocessed magnesium-containing inorganic saline wastewaters comprising the steps of:

5 (a) if required, placing the saline wastewater in a concentration adjustment pond or a tank and adjusting the concentration by dilution or evaporation to contain 5g/L to 100g/L magnesium ion in solution to allow formation of a precipitate;

10 (b) separating the supernatant from the precipitate;

(c) further adjusting the magnesium ion concentration in the supernatant from step (b) to 8-10g/L;

15 (d) if the sulphate content of the solution resulting from step (c) is more than 1.2g/L, reacting the solution from step (c) with either lime $[\text{Ca}(\text{OH})_2]$ or caustic soda $[\text{NaOH}]$ and centrifuging to remove solids;

20 (e) reacting the resultant solution from step (c) or (d) as appropriate with either lime $[\text{Ca}(\text{OH})_2]$ or caustic soda (NaOH) , first under rapid stirring and then slow mixing conditions to produce a slurry
25 dominated by magnesium hydroxide.

(f) thickening the slurry thus produced in a cyclone or centrifuge; and

30 (g) dewatering the resultant magnesium hydroxide slurry.

2. A process according to claim 1 wherein in step (e) of claim 1 said resultant solution is reacted

with caustic soda [NaOH].

3. A process of producing magnesium hydroxide slurry
powder comprising producing a magnesium hydroxide
5 slurry according to claim 1 or 2, dewatering and
drying the slurry to form a crystal compound, and
subjecting the compound to hot-air mixing and/or
grinding to form the powder.

10 DATED this 24th day of December 1996.

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By their Patent Attorneys

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ABSTRACT

A method of manufacturing magnesium hydroxide slurry
and powder from magnesium-containing inorganic saline
wastewaters is disclosed, in which the magnesium
concentration of the saline wastewater is adjusted to
5 5 to 100g/L and precipitate is removed. The magnesium
concentration of the supernatant is then further
adjusted to 8 to 10g/L and is reacted with lime or
caustic soda. The magnesium hydroxide slurry thus
formed is then thickened and dewatered, and optionally
10 powdered.

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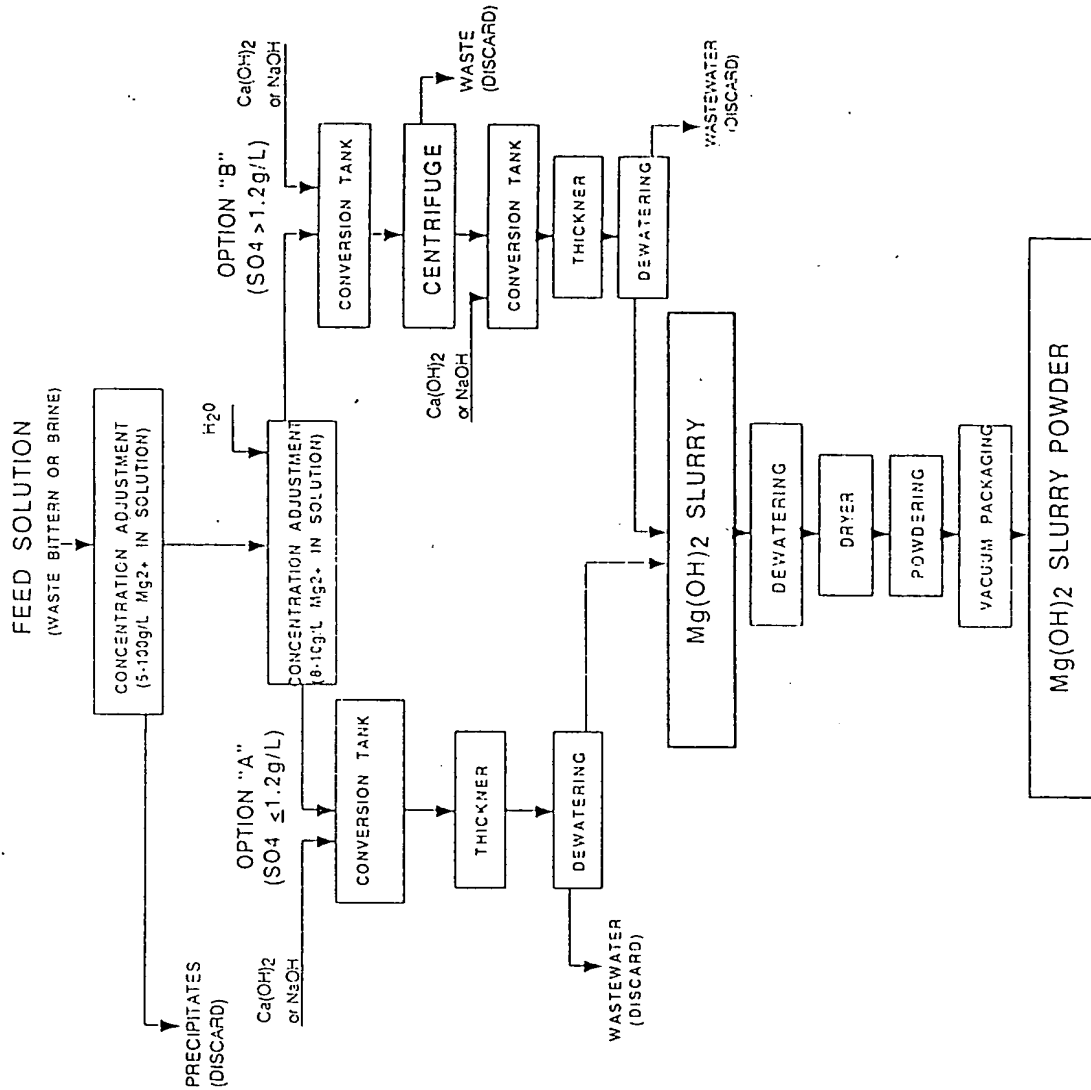


FIGURE 1. PROCESS FLOW CHART FOR MANUFACTURE OF MAGNESIUM-HYDROXIDE SLURRY AND SLURRY POWDER PRODUCTS FROM INORGANIC SALINE WASTEWATERS